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(71) Applicant (for all designated States except US): NED-
ERLANDSE ORGANISATIE VOOR TOEGEPAST-
NATUURWETENS CHAPPELIJK ONDERZOEK
TNO [NL/NL]; Schoemakerstraat 97, NL-2628 VK Delft
(NL).

(72) Inventors; and
(75) Inventors/Applicants (for US only): OONK, Johan
[NL/NL]; Fabianusstraat 12, NL-7333 AC Apeldoorn
(NL). WILLEMS, Franciscus, Petrus, Thomas
[NL/NL]; Veldmoeren 32, NL-4824 JV Breda (NL).
CREIJGHTON, Yves, Lodewijk, Maria [NL/NL];
Annastraat 16, NL-2611 VX Delft (NL).

(74) Agent: WINCKELS, C., S., J., H., F.; Vereenigde,
Nieuwe Parklaan 97, NL-2587 BN Den Haag (NL).

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(54) Title: PURIFICATION OF OFF-GASES FROM GAS-FIRED PLANTS

(57) Abstract: The invention relates to a method and apparatus for purifying off-gasses of gas-fired plants. According to the inven-
tion, just methane or both metane and Nox contents in an off-gas stream of a plant are reduced by contacting the off-gas stream with
a plasma and a catalyst.

Title: Purification of off-gases from gas-fired plants

The invention relates to a method and apparatus for purifying off-gases from gas-fired plants and specifically gas engines.

Gas engines are used *inter alia* for combined heat and power (CHP) generation and for this reason are used to an increasing extent because in
5   this way energy savings, and hence a reduction of CO_2 emissions, can be accomplished. However, a drawback is that small-scale energy generation with CHP gas engines leads to increased emissions of NOx and methane compared with large-scale electricity generation in power stations.

In recent research, the methane problems have been mapped and the
10 methane slip is estimated to be 1.8% of the primary fuel deployment (see: Gastec, 2001: Kwaliteit gasmotoren in Nederland [Gas engine quality in the Netherlands], Gastec report GL/010476, Gastec, Apeldoorn). Methane is a greenhouse gas which, on a weight basis, is 21 times stronger than CO_2 (100 years of integration time, including indirect effects). However, methane slip
15 not only means a contribution to the greenhouse effect, so that the favorable effect of CHP on CO_2 emissions is partly undone again; methane slip also means a reduction of the efficiency of the plant. For all sources of non-CO_2 greenhouse gases, it is currently being investigated what the possibilities are for emission reduction.

20   The NOx emission of a gas engine is considerably higher than that of large-scale energy generation. As a result of increased CHP in the Netherlands, the reduction of acidifying emissions in the Netherlands has slowed down. According to the expectations of the Energy Research Center of the Netherlands (ECN), the CHP engine fleet will grow in the next 10
25 years, and with unchanged regulations NOx emissions will increase proportionally. For Europe a similar growth is expected (see: ECN, 2000: "Mogelijke effecten van NOx-beleid op het warmte-krachtpotentieel"

[Possible effects of NOx policy on the heat-power potential"], ECN report ECN-C--00-111).

Controlling simultaneous NOx and methane emissions by taking engine measures as a rule presents problems in gas engines, since there is a

5   trade-off between methane and NOx emissions and also between energy consumption (CO_2 emission) and NOx emission: engine settings that are favorable in respect of NOx are often unfavorable in respect of methane emission and the energy consumption.

There are a number of possibilities for emission reduction of the

10   individual components, NOx and methane. For NOx emission reduction, engine measures can be taken, but the reduction potential of NOx is limited to about 50% and these measures often result in an increase of the methane emission and a rise of the energy consumption. Another measure for NOx emission reduction is selective catalytic reduction (SCR) of NOx using

15   ammonia or urea. However, on the scale of a gas engine, this is a relatively expensive measure, which moreover requires additional deployment of energy-rich co-reagents. For methane emission reduction there is no proven technology yet, not least because emission requirements for methane are currently still lacking. However, there are a number of possibilities. Engine

20   measures can reduce emissions, but often result in an increase of the NOx emission. Further, methane in the waste gases may be catalytically oxidized, though with limited conversion efficiencies.

Methane-deNOx is proposed as a measure for emission reduction of both components in the case of lean-burn gas engines; however, the measure

25   is not yet available on a realistic or pilot scale, while on a lab scale, efficiencies of NOx emission reduction remain limited under the more realistic conditions to 50% at a maximum (see for instance: Tena E. *et al.*, "Cogeneration and SCR of NOx by natural gas: advances towards commercialisation", NOXCONF 2001, Paris). According to the literature,

30   SCR of NOx with methane does not proceed, or proceeds very slowly, so that

very high contact times (corresponding to very low gas velocities, for

instance expressed in gas hourly space velocity, GHSV) are needed to come

to an acceptable NOx conversion. According to the literature, such low

GHSV values render practical application impossible. Moreover, the

5   catalytic conversion of NOx with CH_4 does not proceed selectively. This

limitation in selectivity is caused by the chemical stability of methane,

which only becomes reactive at elevated temperature. At this elevated

temperature, the catalytic reaction of CH_4 with NOx is not selective

anymore with respect to the non-catalytic reaction with combustion air.

10 Another technology for DeNox is the selective catalytic reduction of NOx

with hydrocarbons, in particular higher hydrocarbons. It proceeds especially

efficiently and selectively when olefins (such as propene) are used as

reductant. In the use of aliphatics (propane, butane), the reaction proceeds

less successfully.

15   A possibility for simultaneous emission reduction of NOx and CH_4

involves the switch to stoichiometric combustion in a gas engine. Given such

a stoichiometric combustion, a three-way catalyst can be used for the

simultaneous removal of NOx, CO and higher hydrocarbons. A

stoichiometric combustion entails a few drawbacks where the heavier-duty

20 engines or engines with a high specific load are concerned, such as a lowered

energetic efficiency and an increased thermal loading.

        In virtually every petrol-powered passenger car driving around at the

moment, a stoichiometric combustion with three-way catalyst is used

successfully. However, because methane in the exhaust gases of a gas

25 engine is much less reactive than the higher hydrocarbons from an engine

running, for instance, on petrol, the efficiency of a three-way catalyst in the

emission reduction of specifically CH_4 remains limited when CNG is used as

fuel.

        US-B1-6 357 223 discloses a method for converting compounds that

30 can poison catalysts in off-gas streams. To this end, these compounds are

reacted with particular active compounds, which are formed from water vapor or other gases, utilizing e.g. UV light or corona discharge. In this method, *inter alia* NO_2 may be formed, which is not desired.

The object of the present invention is to provide a solution to at least
5   a part of the above-mentioned problems and is specifically directed to purification of off-gases from gas-fired plants. The crux of the problem is that methane, compared with other hydrocarbons, is insufficiently reactive. By making use of a plasma, methane is converted into more reactive components, which are better able to perform the desired catalytic reactions.

10   It has been found that off-gas streams of gas-fired plants can be very suitably treated in a step in which so-called plasma assisted catalytic methane conversion is carried out. According to the invention, the methane can be converted with the aid of oxygen (for instance coming from the air; "plasma-assisted oxy-cat"), so that a decrease in the methane content is

15   obtained. Also, the methane can be converted with NOx present in the off-gas ("plasma assisted methane-DeNOx"), whereby a reduction of both NOx and methane can be achieved in that NOx is reduced by the methane present. Accordingly, the invention concerns a method for reducing methane contents, and possibly NOx contents, in an off-gas stream of a gas engine,

20   wherein the off-gas stream is contacted with a plasma and a catalyst. According to the invention, the whole off-gas stream, or at least a substantial part thereof, is subjected to *in situ* plasma treatment, in contrast to the method of US-B1-6 357 223, where only a fraction of the off-gas stream is passed through a corona discharge reactor, a so-called

25   remote corona application.

Moreover, according to the invention, each part of the off-gas is contacted with radicals which are generated, spatially well distributed, in the plasma reactor. Because of short radical recombination times (order of magnitude is typically 1 to 100 microseconds), the radicals produced in a

remote corona discharge will be less effective for the intended chemical conversion of NOx.

Thus, an emission reduction of CH_4 and if desired NOx is obtained, moreover with possibilities of increasing the total efficiency (sum of energetic and thermal efficiency) of the gas-fired plant. According to the invention, it is for instance possible, in a gas engine, to raise the compression ratio, to advance ignition, or to set the air/fuel ratio such that a lower fuel consumption is realized and the energy demand of the plasma is compensated. This setting yields a lower hydrocarbon emission and the increase of the NOx is undone by the plasma assisted catalytic reduction of NOx.

Fig. 1 schematically shows two embodiments according to the invention. In the embodiment according to Fig. 1A, the off-gas of a gas engine is first passed through a plasma reactor and subsequently through the catalyst bed. In the embodiment schematically represented in Fig. 1B, the plasma reactor and the catalyst bed are integrated.

The invention is specifically effective because the exhaust gas in most cases contains sufficient methane to reduce NOx completely. Should this not be the case, the methane content in the exhaust gas can be increased relatively simply through a different setting of the plant.

Although it cannot be stated with certainty what the most active components are that play a role in the chemistry of the present invention, it is assumed – without wishing to be bound to any theory – that according to the invention the following reactions occur.

In the plasma, there are free electrons with a characteristic electron energy in the range of 1-10 eV. The free electrons generate a large variety of chemically reactive particles in the exhaust gas, such as radicals (OH) and ions (CH_3^-). CH_4 is converted both in a direct manner by electrons and in an indirect manner by radicals and ions. An occurring direct reaction is dissociative coupling of electrons with CH_4:

$$CH_4 \; + \; e^- \qquad \rightarrow \quad CH_3^{\cdot} \; + \quad H \qquad (1)$$

$$CH_4 \; + O_2 \; + \quad e^- \quad \rightarrow \quad HO_2 \; + \quad CH_xO_y \qquad (2)$$

In addition, in the plasma reactor, nitrogen monoxide (NO) is
5   converted according to:

$$NO \qquad + \qquad HO_2 \qquad \rightarrow \quad NO_2 \; + OH \qquad (3)$$

The reduction takes place on the catalyst:

10

$$NO_2 \qquad + \qquad CH_xO_y \qquad \rightarrow \quad N_2 \; + \; CO_2 + H_2O \quad (4)$$

Although a plasma reactor is capable of activating gas molecules, the
reduction of NOx to N_2 cannot be effectively accomplished with it. Similarly,
15   known catalysts for catalytic conversion of NOx with the aid of
hydrocarbons under realistic conditions are not suitable for the conversion
of methane and NOx to water, CO_2 and nitrogen. Surprisingly, with the
combination according to the invention, it has been found that an effective
reduction of NOx with methane can be achieved.
20   For catalytic conversion of NOx with methane, it is important that
direct conversion of methane to CO_2 proceeds in a controlled manner,
because CO_2 is not reactive anymore in the catalytic conversion of NOx;
however, complete conversion of CH_4, either in reaction with NOx or in
reaction with O_2 from combustion air remains desired. According to the
25   invention, the controlled conversion of CH_4 is accomplished by use of the
plasma. Again without wishing to be bound to any theory, it is assumed that
the first oxidation step of CH_4 in the presence of plasma is no longer
velocity-determinative (whereas this step *is* velocity-determinative in
"conventional" oxidation of CH_4, that is, oxidation – combustion – without

use of a plasma, because this first oxidation of CH_4 then has the highest
activation energy). Through use of the plasma, the forming reactions of all
oxidation products from methane (CH_3OH, CH_2O, CO, H_2) have a more or
less equal, low, activation energy and these components will be formed in a
5   more selective manner.

According to the invention, the plasma is generated by ionization of
the components in the gases by means of a high electrical or electromagnetic
field (for instance generated by microwaves). A suitable plasma reactor
provides discharges at relatively high electrical fields (as a rule ca. 1-100
10   kV/cm, typically 10 kV/cm). As a result, free electrons, reactive radicals, ions
and partially oxygenated compounds (CH_xO_y) are formed in the gaseous
phase. The relatively high electrical fields are necessary because the
pressure is also relatively high, viz. approximately atmospheric (this is high
compared with customary plasma applications). Preferably, an AC voltage is
15   used, which preferably has a frequency of 10 Hz to 100 kHz, typically ca. 1
kHz. Preferably, the electrical field is generated between a pair of
electrodes, at least one of the electrodes being fully insulated from the
off-gas by an electrically insulating layer consisting of, for instance, glass or
ceramic. Because of the homogeneous spatial distribution of plasma
20   filaments, which enable an effective *in situ* treatment of the complete gas
stream, the power density (W/cm³) of the plasma can remain limited. The
power density of the plasma is determined to a large extent by the frequency
of the plasma. This frequency is preferably below 1 kHz.

Preferably, the plasma is maintained with the aid of a partial
25   discharge. Preferably, the partial discharge is generated by the use of a
dielectric, such as ceramic or glass, which, preferably completely, covers one
or more of the electrodes in the plasma reactor. In this way, a more compact
apparatus can be obtained.

The temperature for performing the plasma reactions and the
30   catalytic reactions are preferably set at 300 - 500 °C, but this may vary for

different applications. For use in the automobile industry, a temperature of approximately 350 °C is optimal. For combined heat and power systems, this temperature may be higher, for instance 360 - 370 °C.

5   As catalyst, in principle all known three-way catalysts, hydrocarbon-NOx-SCR catalysts or oxidation catalysts are suitable, in particular catalysts based on zeolites (which may or may not be ion exchanged) or metal oxides such as γ- alumina, if desired activated with metals as silver, indium, platinum, palladium, copper or rhodium. In the choice of a suitable catalyst system, the following considerations can play a role. Suitable

10   catalysts for use in CH_4-deNOx or methane oxidation must meet a number of requirements in respect of activity, stability and selectivity.

The catalysts should be active in a relatively wide temperature range of preferably about 200 °C to about 400 °C. It is requisite that sufficient conversion be obtained at high GHSV, typically greater than 50 000 h^{-1},

15   running up to approximately 150 000 h^{-1} or more. The catalyst systems should be able to adsorb and activate the reactants. Relevant in that respect are *inter alia* a sufficiently high pore volume, a sufficiently high specific surface area, a sufficient extent of dispersion of the catalytically active sites and a suitable acidity.

20   Suitable catalyst systems contribute to the following desired reactions 1) to 5).

Oxidation	1) $NO + O_2$	$\rightarrow$	NO_2
	2) $C_xH_y + O_2$	$\rightarrow$	$C_xH_yO_z$ of CO
H2 generation	3) $C_xH_y + H_2O$	$\rightarrow$	$H_2 + CO + CO_2$
NOx reduction	4) $NO/NO_2 + C_xH_y/C_xH_yO_z/CO$	$\rightarrow$	$N_2 + CO_2 + H_2O$
Hydrocarbon oxidation:	5) $CH_2, C_xH_yO_z$	$\rightarrow$	CO_2 and H_2O

The following undesired reactions 6) to 11) should be prevented as

30   much as possible:

NOx conversion	6) NO_2	$\rightarrow$	$NO + O_2$
	7) NO	$\rightarrow$	N_2O
Oxidation	8) $NO_2 + C_xH_y$	$\rightarrow$	$CO, CO_2 + NO$
	9) SO_2	$\rightarrow$	$SO_3 (\rightarrow H_2SO_4 \text{ with } H_2O)$
	10) C_xH_y	$\rightarrow$	CO_2
Deposition	11) C_xH_y	$\rightarrow$	C

As regards the selectivity, the catalyst system used should preferably promote the oxidation of hydrocarbons, without this leading to non-selective combustion. In other words, preferably, eventually reaction 4) is maximized, while reactions 6) to 11) are minimized. The catalyst system should also be stable to a sufficient extent at the temperature used, especially in the presence of components such as H_2O, SO_2, coke, Cl, As, P, Si. Also, the catalyst system used should offer sufficient resistance to mechanical erosion.

Very suitable catalyst systems that can meet the above-mentioned requirements are catalysts based on γ-Al_2O_3. γ-Al_2O_3 is active in CH_4-SCR, although according to the prior art this holds specifically at high temperatures. According to the invention, however, NOx is for a considerable part present in the form of NO_2, which proves to be considerably more reactive than NO. γ-Al_2O_3 moreover offers a good sulfur and water tolerance and can easily be modified with different metals and additives.

Very suitable as catalyst support for CH_4-deNOx under lean-burn conditions are inter alia different types of Al_2O_3, zeolites, in particular H-Zeolites (H-USY, H- FER, H-ZSM5, H-MOR), oxides such as ZrO_2, Ga_2O_3, perovskite and combinations (mixtures or layered structures) thereof. Perovskite is suitable in particular because it enables the simultaneous removal of NOx and soot particles. As active phases on these supports, metals, metal ions and metal oxides can be used. Very suitable are silver

and platinum. Silver is specifically suited for reducing NO_2. Platinum is
suitable in particular because of the high activity at low temperatures.
Other suitable metals are In, Ce, Au, Fe, Pd and Sn, because these are
capable of reducing NO_2 very effectively. Finally, BaO-based systems are

5   mentioned. This so-called storage reduction catalyst can bind NOx in the
form of nitrates and in this way enhance the activity of the catalyst system.

A suitable catalyst system for plasma-assisted deNox in lean burn gas
engines comprises, for instance, Ag/Al_2O_3 or Ag/H-Zeolite. Such a system
gives a high conversion, possesses a good stability and is especially active

10   for the conversion of NOx with partially oxidized hydrocarbons (for instance
MeOH). Other examples include In/Zeolite In_2O_3/Ga_2O_3, Pt/Al_2O_3, etc.

A suitable catalyst system for plasma-assisted methane oxidation in
lean-burn gas engines comprises, for instance, Ag or Pt on Al_2O_3 or
H-Zeolite support. However, also other catalysts that are proposed by others

15   as oxidation catalyst for hydrocarbons can be suitable.

For plasma-assisted deNOx in stoichiometric engines, specifically all
three-way catalysts are suitable, such as they have currently been
developed by third parties, and are mostly based on rhodium, platinum or
platinum on an alumina support, with sometimes additions of cerium,

20   lanthanum, zirconium or cerium.

In the embodiment schematically represented in Fig. 1A, the
off-gas (1) to be cleaned is first passed through a plasma reactor, which is
connected at (2) with a voltage source. Next, the gas stream passes the
catalyst bed. The cleaned gas is obtained at (3).

25   The reference numerals in Fig. 1B have corresponding meanings to
Fig. 1A. In this embodiment, plasma reactor and catalyst bed are
integrated. This provides two advantages over the sequential embodiment of
Fig. 1A: in the first place, a more compact plant is obtained. In the second
place, any reverse reactions (for instance of the activated NO_2 to NO) are

prevented because the more active components can react away directly over the catalyst.

CLAIMS

1.   A method for reducing the methane content in an off-gas stream of a gas-fired plant, wherein at least a portion of said off-gas stream is contacted with a plasma and a catalyst.

2.   A method according to claim 1, wherein further the NOx content of said off-gas stream is reduced.

3.   A method according to any one of the preceding claims, wherein said plasma is generated by the use of an electrical or an electromagnetic field.

4.   A method according to claim 3, wherein the plasma is generated by use of an electrical field of 1-100 kV/cm.

5.   A method according to any one of the preceding claims, wherein the plasma is generated by means of an alternating voltage of a frequency of 100 Hz to 100 kHz.

6.   A method according to any one of the preceding claims, wherein the plasma is maintained with the aid of a partial discharge.

7.   A method according to claim 6, wherein the partial discharge is generated by use of a dielectric.

8.   A method according to any one of the preceding claims, wherein the whole off-gas stream or virtually the whole off-gas stream is contacted with said plasma and said catalyst.

9.   A method according to any one of the preceding claims, which is carried out at a temperature of 300 - 500 °C.

10.   A method according to any one of the preceding claims, wherein said catalyst comprises Al_2O_3, zeolite, ZrO_2, Ga_2O_3, TiO_2, WO_3, perovskite or combinations thereof.

11.   A method according to claim 8, wherein said catalyst comprises γ-Al_2O_3.

12.   A method according to any one of the preceding claims, wherein said catalyst is a three-way catalyst, which comprises Rh, Pt or Pd on Al_2O_3 support, if desired with additions of Ce, La, Zr or Ce.

13.   A method according to any one of the preceding claims, wherein said catalyst is an oxidation catalyst, which comprises Ag or Pt on a metal oxide support.
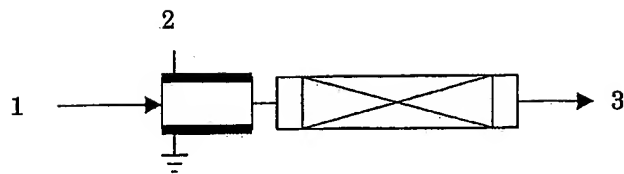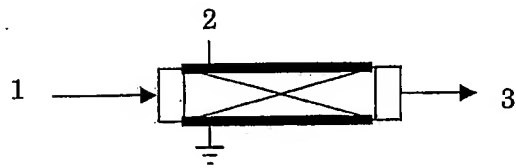
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Fig. 1A

Fig. 1B

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   B01D53/86   B01D53/32   F01N3/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   B01D   F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 357 223 B1 (CAREN ET AL) 19 March 2002 (2002-03-19) column 5, line 15 - column 13, line 65	1-13
A	US 5 254 231 A (HEATH ET AL) 19 October 1993 (1993-10-19) column 3, line 1 - column 3, line 18	1
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☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

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